Kinetics of Oxidation of Indigo Carmine by N-Sodio-N-Bromotoluenesulfonamide in Acidic Buffer Medium

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ABSTRACT: The kinetics of oxidation of indigo carmine (IC) by N-sodio-N-bromotoluenesulfonamide or bromamine-T (BAT) in pH 5 buffer medium has been investigated at 30°C using spectrophotometry at 610 nm. The reaction rate shows dependencies of first-order on $[IC]_0$, second-order on $[BAT]_0$, fractional order on $[H^+]$, and inverse first-order on [*p*-toluenesulfonamide]. The addition of chloride and bromide ions, and the variation of ionic strength of the medium have no influence on the reaction rate. There is a negative effect of the dielectric constant of the solvent. Activation parameters have been calculated. A single-pathway mechanism for the reaction, consistent with the kinetic data, has been proposed. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 453–459, 1997

INTRODUCTION

Indigo carmine or IC (5,5′-indigodisulfonic acid, disodium salt) finds applications as a redox indicator in analytical chemistry and as a microscopic stain in biology [1]. The chemistry of IC and its derivatives has been reviewed by Rodd [2]. Although there are several analytical methods available for IC [3,4], only a few studies of the kinetics of IC oxidation are reported in the literature. Several studies on the mechanistic aspects of oxidation of diverse organic substrates including IC by aromatic haloamines have been reported by us and others [5–11]. Bromamine-T or BAT (*p*-Me-C6H4SO2NBrNa $3H_2O$) is a haloamine containing a positive bromine implicated in the reaction of functional groups of the substrates. To our knowledge, however, there is no report on the kinetics of the IC-BAT reaction. In the present article, we report the spectrophotometrically monitored kinetics of oxidation of IC by BAT in pH 5 buffer medium with an attempt to elucidate the reaction mechanism.

EXPERIMENTAL

Bromamine-T Solution

The oxidant, BAT, was prepared and purified using the method of Nair and Indrasenan [12]. Its purity was determined by iodometry and by its UV, IR, and ^1H- and ^{13}C-NMR spectra [4]. An aqueous solution of

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BAT was prepared, standardized periodically by the iodometric method [4], and preserved in an amber-colored bottle until further use.

Indigo Carmine Solution

As the substrate, IC, is prone to aerial oxidation and light, aqueous solutions of IC (E. Merck) were freshly prepared and used.

Buffer System

A pH 5 buffer solution (0.10 M) of potassium hydrogen phthalate and NaOH was prepared and its pH value checked with a pH meter [13].

All chemicals used were of analytical grade. A constant ionic strength in the reaction mixture was maintained by adding a required amount of 5.0 M $NaClO_4$ solution. Triply distilled water was used for preparing aqueous solutions.

Kinetic Procedure

Kinetic runs were performed under pseudo-first-order conditions of $[BAT]_0 >> [IC]_0$ at 30°C. For each run, requisite amounts of solutions of IC, $NaClO_4$, and a buffer of known pH were taken in a stoppered Pyrex glass tube whose outer surfaces were coated black. A required amount of water was added to maintain a constant total volume in all runs. The tube was thermostated in a water bath at a given temperature. The reaction was initiated by adding a measured amount of preequilibrated BAT solution and shaken periodically for uniform concentration. The course of the reaction was monitored spectrophotometrically by measuring the absorbance of IC at its λ_{max} of 610 nm at regular time intervals for three half-lives. The pseudo-first-order rate constants, k', calculated were reproducible within $\pm 3\%$. Since the total ionic strength maintained was 0.2 M, molar concentrations were used in the expression of rate constants instead of activities, in first approximation, neglecting the activity coefficients. Regression analysis of the experimental data was carried out on a TDC-316 computer and on an EC-72 statistical calculator.

Reaction Stoichiometry

Varying ratios of the oxidant (BAT) to IC in pH 5 buffer medium were equilibrated at 30°C for 12 h. Aliquots of the reaction mixture were iodometrically titrated with a standard thiosulfate solution, using starch indicator, to determine the concentrations of unchanged BAT. The mole ratio (number of moles of BAT consumed per mole of IC) was calculated.

Product Analysis

The presence of *p*-toluenesulfonamide or PTS, which is the reduction product of BAT, was detected by paper chromatography [4]. The oxidation product of IC, sodium salt of sulfonated anthranilic acid (SAA), was analyzed [4]. The SAA present in the reaction mixture was quantitatively determined using a standard method involving its precipitation as zinc(II) salt, $Zn(C_7H_5O_5NSNa)_2$ [14]. The recovery of SAA from different reaction mixtures in pH 5 buffer was in the range 85–95%. Another product, CO_2, was detected by the conventional lime water test. Attempts to quantitate the amount of CO_2 evolved were unsuccessful.

Test for Free Radicals

The addition of the reaction mixtures, in the dark, to olefinic compounds such as acrylonitrile and methyl methacrylate failed to initiate polymerization of the monomers by the free radicals formed in situ. Proper control experiments with the solutions of BAT and IC were also performed under the same experimental conditions.

RESULTS

Reaction Stoichiometry

The results of IC reaction with BAT showed a definite stoichiometry of 1:4 (i.e., four moles of the oxidant reacted with every mole of IC) forming SAA and CO_2 as oxidation products and *p*-toluenesulfonamide (PTS) and Br^- as reduction products.

Kinetics

Effects of Varying Reactant Concentrations on the Rate. Under pseudo-first-order conditions of $[BAT]_0 >> [IC]_0$, at constant $[BAT]_0$, pH, and temperature, the plots of log (A_0/A_t) vs. time were linear ($r > 0.9989$; $s \leq 0.05$) indicating a first-order dependence of the reaction rate on $[IC]_0$. A_0 and A_t are the absorbances of the reaction mixture at time intervals of zero and *t*, respectively. The pseudo-first-order rate constants, k', obtained at 30°C are independent of $[IC]_0$ further confirming the first-order dependence on $[IC]_0$ (Table I). At constant pH, $[IC]_0$, ionic strength, and temperature, the rate increased with increasing $[BAT]_0$ (Table I). Furthermore, a plot of log k' vs. log

Table I Effect of Varying Reactant Concentrations on the Reaction Rate
λ_{max} = 610 nm; μ = 0.20 M; pH = 5.0; and temp. = 303 K

$[BAT]_o \times 10^4$ (M)	$[IC]_o \times 10^5$ (M)	$k' \times 10^3$ (s^{-1})
1.20	5.00	1.87
1.40	5.00	2.50
1.60	5.00	3.32
1.80	5.00	4.22
2.00	5.00	5.12
1.60	3.00	3.30
1.60	4.00	3.28
1.60	6.00	3.35
1.60	7.00	3.32

$[BAT]_0$ was linear (Fig. 1; r = 0.9997, s $\leq$ 0.02) with a slope of 2.0 showing a second-order dependence on [BAT].

Effect of pH on the Rate

The reaction rate decreased with increasing pH of the medium (Table II). A plot of log k' vs. log $[H^+]$ was linear with a slope of 0.71 (Fig. 2; r = 0.991) showing a fractional-order dependence on $[H^+]$.

Table II Effect of pH on the Reaction Rate
λ_{max} = 610 nm; $[BAT]_o = 1.60 \times 10^{-4}$ M; $[IC]_o = 5.00 \times 10^{-5}$ M; μ = 0.20 M; and temp. = 303 K

pH	$k' \times 10^3/(s^{-1})$
4.2	13.05
4.6	5.98
5.0	3.32
5.4	1.34
5.8	1.00

Effect of PTS Concentration on the Rate

Addition of the reaction product, PTS ($2.0 \times 10^{-4} - 1.0 \times 10^{-3}$ M), to the reaction mixture retarded the reaction rate (Table III). A plot of log k' vs. log [PTS] was linear (r > 0.9986) with a slope of −1.07.

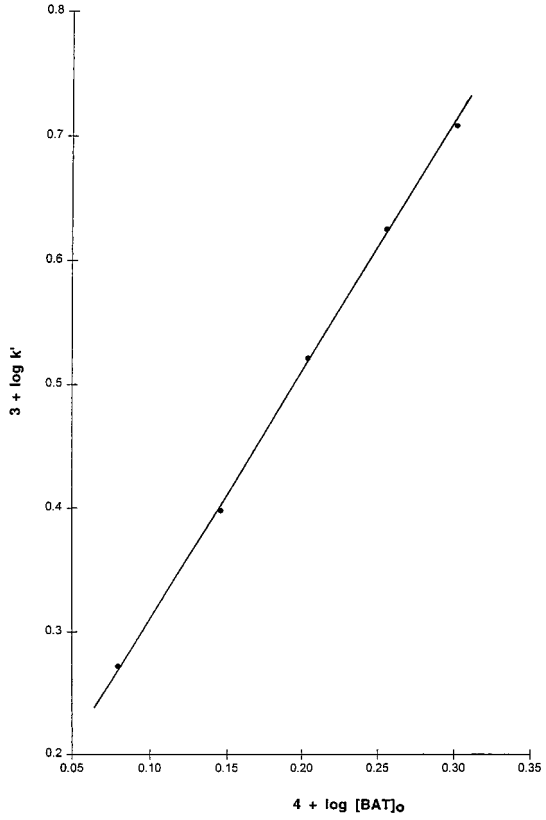


Figure 1 A plot of log k' vs. log $[BAT]_0$: $[IC]_0 = 5.00 \times 10^{-4}$ M; pH 5.0; μ = 0.20 M; λ_{max} = 610 nm; and temp. = 30 ± 0.1°C.

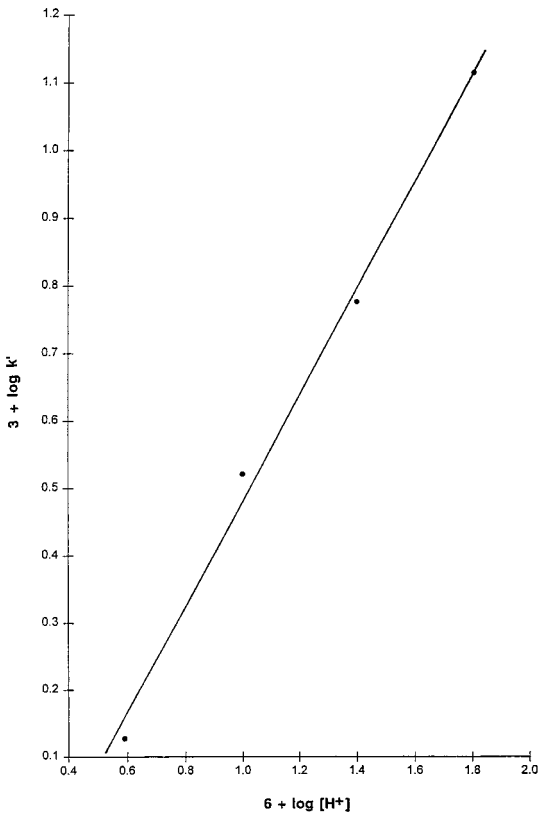


Figure 2 A plot of log k' vs. log $[H^+]$: $[BAT]_0 = 1.60 \times 10^{-4}$ M; $[IC]_0 = 5.00 \times 10^{-5}$ M; μ = 0.20 M; λ_{max} = 610 nm; and temp. = 30 ± 0.1°C.

Table III Effect of Varying *p*-Toluenesulfonamide (PTS) Concentration on the Reaction Rate
λ_{max} = 610 nm; $[BAT]_o = 1.60 \times 10^{-4}$ M; $[IC]_o = 5.00 \times 10^{-5}$ M; pH = 5.0; μ = 0.20 M; and temp = 303 K

[PTS] × 10^4/(M)	$k' \times 10^4/(s^{-1})$
0.0	33.20
5.0	30.00
10.0	15.11
15.0	9.82
20.0	6.72

Effects of Halide Ion and Ionic Strength on the Rate

Addition of chloride or bromide ions ($5.0 \times 10^{-5} - 1.5 \times 10^{-4}$ M), in the form of NaCl or NaBr, to the reaction mixture had no effect on the rate. Ionic strength of the reaction medium varied by adding $NaClO_4$ (0.050–0.40 M overall) did not affect the rate.

Effect of Varying Dielectric Constant (D) of Solvent on the Rate

The effect of D on the reaction rate was studied by varying MeOH content (0–20% V/V) in pH 5 buffer medium. The rate decreased with an increase in MeOH content of the medium. Furthermore, a plot of log k' vs. 1/D gave a straight line with a negative slope (r = 0.9956). This effect is in conformity with the Amis concept for dipole–dipole or dipole–ion interactions [15].

Effect of Temperature on the Rate

The reaction was studied at different temperatures, 298 K to 313 K, while keeping the $[BAT]_0$ and other experimental conditions constant. The rate constants are presented in Table IV. The activation parameters (Table IV) were calculated from the slopes and intercepts of the Arrhenius and Eyring plots of log k' vs. $1/T$ and log (k'/T) vs. $1/T$), respectively (r = 0.9997 for both plots).

Table IV Temperature Dependence of the Reaction Rate and Activation Parameters for the Indigo Carmine Oxidation by Bromamine-T
λ_{max} = 610 nm; $[BAT]_o = 1.60 \times 10^{-4}$ M; $[IC]_o = 5.00 \times 10^{-5}$ M; pH = 5.0; μ = 0.20 M

Temperature (K)	$k' \times 10^3/(s^{-1})$	Activation Parameters
298	2.51	Ea : 39.75 kJ mol^{-1}
303	3.32	$\Delta H^{\neq}$: 37.21 kJ mol^{-1}
308	4.20	$\Delta S^{\neq}$: −170.0 JK^{-1} mol^{-1}
313	5.45	$\Delta G^{\neq}$: 89.13 kJ mol^{-1}

Detection of Free Radicals

Tests performed using olefinic monomers were negative indicating the absence of free-radical formation in the reaction mixtures of BAT and IC.

DISCUSSION

Reaction Stoichiometry

The results of IC reaction with BAT showed a definite stoichiometry of 1:4 (i.e., four moles of the oxidant reacted with every mole of IC) forming SAA and CO_2 as oxidation products and *p*-toluenesulfonamide (PTS) and Br^- as reduction products. The stoichiometric reaction can be represented as in eq. (1) below.

$$\underset{(IC)}{C_{16}H_8O_8S_2N_2Na_2} + 4\ \underset{(\text{anion of BAT})}{ArSO_2NBr^-} + 6\ H_2O \longrightarrow 2\ \underset{(SAA)}{C_7H_6O_5NSNa} + 2\ CO_2 + 4\ \underset{(PTS)}{ArSO_2NH_2} + 4\ Br^- \quad (1)$$

where Ar = *p*-Me—C_6H_4— and the structures of IC and SAA are as shown in Scheme II.

Kinetics

Bromamine-T ($ArSO_2NBrNa\ 3H_2O$), like chloramine-T (CAT) which behaves as an electrolyte [16], dissociates in aqueous solutions to furnish an anion (eq. (2)). This anion undergoes protonation in acid medium to form the free acid, $ArSO_2NHBr$, as in eq. (3). Although the free acid has not been isolated, the conductometric studies of CAT have provided ample evidence of its formation [16,17]. In acid medium, the free acid undergoes disproportionation to form dibromamine-T ($ArSO_2NBr_2$) and *p*-toluenesulfonamide ($ArSO_2NH_2$) (eq. (4)). Dibromamine-T or DBT and $ArSO_2NHBr$ hydrolyze to give HOBr as one of the products [eqs. (5) and (6)].

$$ArSO_2NBrNa \rightleftharpoons ArSO_2NBr^- + Na^+ \quad (2)$$

$$ArSO_2NBr^- + H^+ \underset{(\text{fast})}{\rightleftharpoons} ArSO_2NHBr \quad (3)$$

$$2\ ArSO_2NHBr \rightleftharpoons ArSO_2NBr_2 + ArSO_2NH_2 \quad (4)$$

$$ArSO_2NBr_2 + H_2O \rightleftharpoons ArSO_2NHBr + HOBr \quad (5)$$

$$ArSO_2NHBr + H_2O \rightleftharpoons ArSO_2NH_2 + HOBr \quad (6)$$

The possible reactive oxidizing species in acidified BAT solutions are, therefore, $ArSO_2NHBr$, $ArSO_2NBr_2$, and HOBr. In the present study of IC oxidation, the reaction shows a second-order in $[BAT]_0$ and a retardation by the added PTS ($ArSO_2NH_2$), i.e., an inverse first-order on $[PTS]_0$, indicating the involvement of $ArSO_2NBr_2$ as the kinetically active species in a fast preequilibrium. Additionally, the reaction rate shows dependencies of a first-order on $[IC]_0$ and a fractional-order on $[H^+]$. Based on the preceding discussion, a mechanism (Scheme I) is proposed to account for the experimental observations.

$$ArSO_2NBr^- + H^+ \overset{K_1}{\rightleftharpoons} ArSO_2NHBr \quad \text{(fast)} \quad \text{(i)}$$

$$2\,ArSO_2NHBr \overset{K_2}{\rightleftharpoons} \underset{\text{(DBT)}}{ArSO_2NBr_2} + \underset{\text{(PTS)}}{ArSO_2NH_2} \quad \text{(fast)} \quad \text{(ii)}$$

$$\underset{\text{(DBT)}}{ArSO_2NBr_2} + IC \xrightarrow{k_3} \underset{\text{(complex)}}{X} \quad \text{(slow)} \quad \text{(iii)}$$

$$ArSO_2NBr_2 + X \rightarrow\rightarrow \text{products} \quad \text{(fast)} \quad \text{(iv)}$$

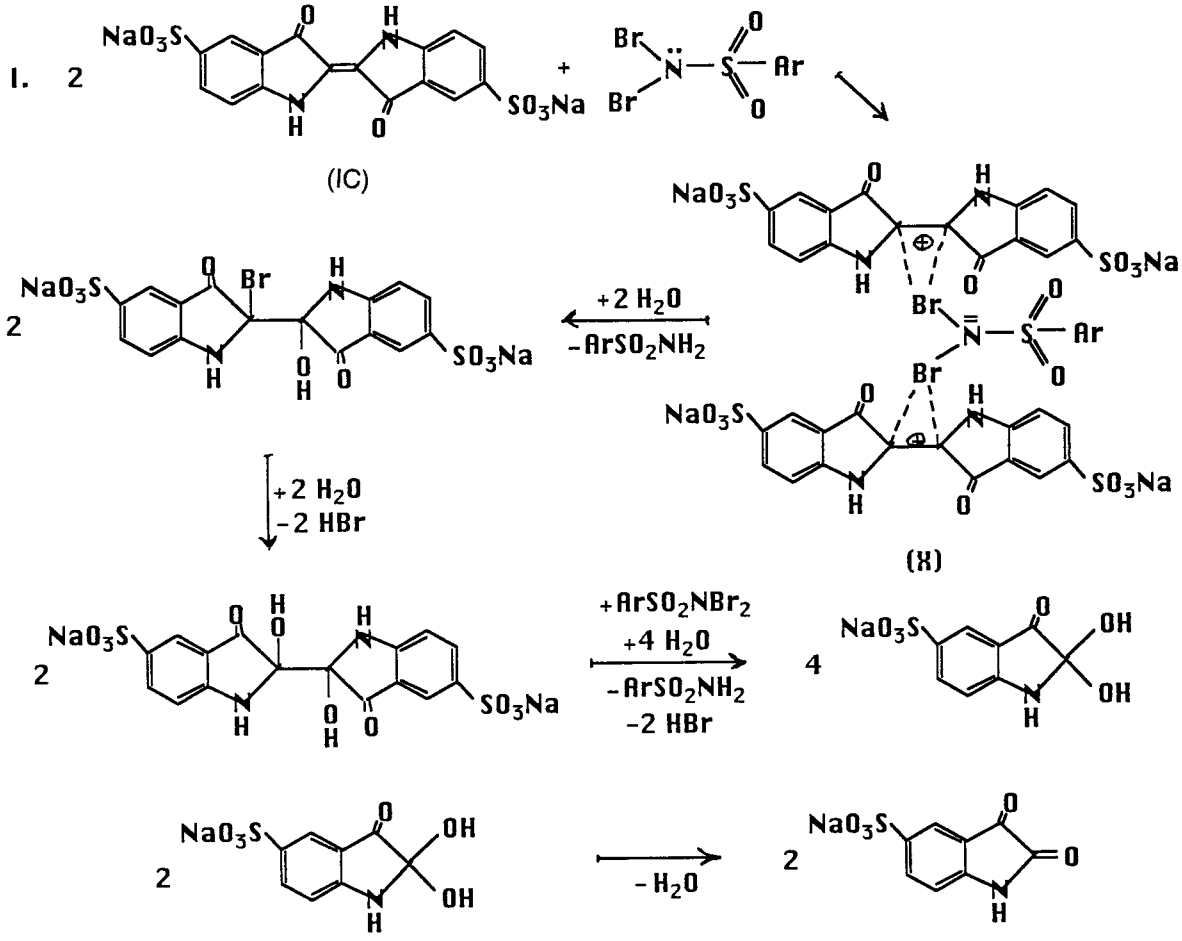
Scheme I

In Scheme I, X represents the indigo carmine-dibromamine-T (DBT) complex intermediate whose possible structure is shown in Scheme II. A detailed mechanism showing the electron transfer reaction between IC and DBT or $ArSO_2NBr_2$ (an active oxidizing species of BAT) is presented in Scheme II. An electrophilic attack of Br^+ of $ArSO_2NBr_2$ across the carbon-carbon double bond of IC leads to the formation of the complex X which on hydrolysis yields a bromohydrin. The bromohydrin intermediate undergoes further interactions with water to form a diol intermediate which on interaction with the oxidant and water undergoes a carbon-carbon bond rupture and dehydration to form 5-isatin sulfonate. The isatin sulfonate intermediate undergoes further oxidation with $ArSO_2NBr_2$ followed by nucleophilic attacks by water and intramolecular rearrangements to form the end product, sulfonated anthranilic acid (SAA).

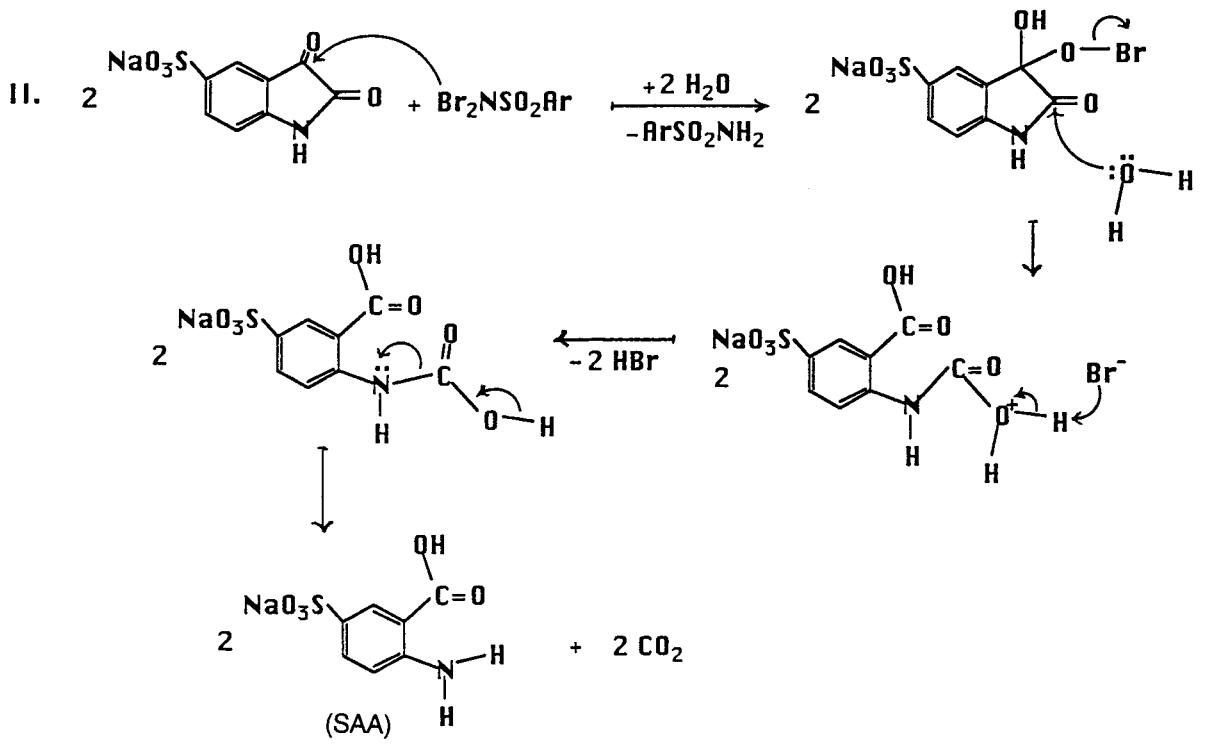
Scheme I leads to the rate law as follows:

$$\text{rate} = d[IC]_{/dt} = k_3\,[DBT][IC] \qquad (7)$$

The total effective concentration of BAT is given by



Scheme II



Here Ar = p-MeC_6H_4- for dibromamine-T (DBT) and p-toluenesulfonamide (PTS)

Scheme II *Continued*

$$[BAT]_t = [ArSO_2NBr^-] + [ArSO_2NHBr] + [DBT] \quad (8)$$

From equilibria (i) and (ii) in Scheme I,

$$[ArSO_2NBr^-] = \frac{[ArSO_2NHBr]}{K_1[H^+]}; \quad (9)$$

$$[ArSO_2NHBr] = \frac{\{[DBT][PTS]\}^{1/2}}{K_2^{1/2}} \quad (10)$$

Substitution for $[ArSO_2NHBr]$ from eq. (10) in eq. (9) gives

$$[ArSO_2NBr^-] = \frac{\{[DBT][PTS]\}^{1/2}}{K_2^{1/2}\,K_1[H^+]} \quad (11)$$

By solving for $[BAT]_t$ of eq. (8) using eqs. (10) and (11), one gets

$$[BAT]_t = \frac{[DBT]\{[PTS]^{1/2} + K_1[H^+][PTS]^{1/2} + K_1K_2^{1/2}[H^+][DBT]^{1/2}\}}{K_1K_2^{1/2}[H^+][DBT]^{1/2}}$$

or

$$[DBT] = \frac{K_1K_2^{1/2}[H^+][BAT]_t[DBT]^{1/2}}{[PTS]^{1/2} + K_1[H^+][PTS]^{1/2} + K_1K_2^{1/2}[H^+][DBT]^{1/2}} \quad (12)$$

Since in acid medium BAT, like chloramine-T, exists predominantly as $ArSO_2NHBr$, $[ArSO_2NHBr] \approx [BAT]_t$. Therefore, eq. (10) takes the form,

$$[DBT]^{1/2} = \frac{K_2^{1/2}[BAT]_t}{[PTS]^{1/2}}$$

By substituting for $[DBT]^{1/2}$ in eq. (12), one gets

$$[DBT] = \frac{K_1K_2[BAT]_t^2[H^+]}{[PTS]\{1 + K_1[H^+]\} + K_1K_2[BAT]_t[H^+]} \quad (13)$$

Substitution for [DBT] in eq. (7) leads to eq. (14),

$$\text{rate} = \frac{K_1K_2k_3[\text{IC}][\text{BAT}]_t^2[\text{H}^+]}{[\text{PTS}]\{1 + K_1[\text{H}^+]\} + K_1K_2([\text{H}^+][\text{BAT}]_t} \quad (14)$$

Assuming that the magnitude of the third term is smaller than that of the first or the second term, in the denominator of eq. (14), the third term can be neglected. Therefore, the above rate law reduces to eq. (15) below.

$$\text{rate} = \frac{K_1K_2k_3[\text{IC}][\text{BAT}]_t^2[\text{H}^+]}{[\text{PTS}]\{1 + K_1[\text{H}^+]\}} \quad (15)$$

This rate law supports the following observed orders in participants: 1.0 for IC, 2.0 for BAT, fractional for H^+, and -1.0 for PTS. If one assumes that the values of protonation constant K_1 and disproportionation constant K_2 of chloramine-T are nearly equal and close to those of BAT, then $K_1(\text{BAT}) \approx K_2(\text{BAT}) \approx 0.154$ at pH 5.0 and 303 K [9]. Using these approximate equilibrium constant values of BAT, it can be shown that the third term tends to be the smallest of the three terms in eq. (14) justifying its omission.

Amis [15] has shown that, for a limiting case of zero angle of approach between two dipoles or between an ion and a dipole, a plot of log k' vs. 1/D (where D = dielectric constant of the solvent medium) has a negative slope for dipole–dipole or anion–dipole interactions and a positive slope for cation–dipole interactions in the rds. In the present study, the observed negative effect of D supports the proposed dipole–dipole interactions in the rds in Scheme I of the mechanism.

The moderate value of enthalpy of activation ($\Delta H^{\neq}$) is supportive of the proposed mechanism in Schemes I and II. The highly negative entropy of activation ($\Delta S^{\neq}$) indicates the formation of a rigid transition state by an associative process.

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